

12

EUROPEAN PATENT APPLICATION

21 Application number: 87309842.0

51 Int. Cl.⁴: C 11 D 3/39

22 Date of filing: 06.11.87

30 Priority: 06.11.86 US 928065

43 Date of publication of application:
11.05.88 Bulletin 88/19

84 Designated Contracting States:
BE CH DE ES FR GB GR IT LI LU NL SE

71 Applicant: The Clorox Company
1221 Broadway
Oakland California 94612 (US)

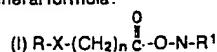
72 Inventor: Zielske, Alfred G.
2282 Via Espada
Pleasanton California 94566 (US)

74 Representative: Froud, Clive et al
Elkington and Fife High Holborn House 52/54 High
Holborn
London WC1V 6SH (GB)

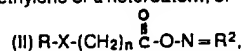
54 Bleaching compositions comprising peracid precursors.

57 A bleaching composition characterised in that it comprises:

(a) a peracid precursor corresponding to the following general formula:



wherein R represents C₁-C₂₀ alkyl, alkoxy, or cycloalkyl; R¹ represents a group which contains at least one carbon atom which is singly bonded directly to N; n represents an integer of from 1 to 6; and X represents methylene or a heteroatom; or



wherein n is as defined above; R² represents a group which contains a carbon atom doubly bonded directly to N, and, either X represents a heteroatom, R represents C₄-C₁₇ alkyl, or both;

(b) a bleach-effective amount of a source of hydrogen peroxide;

and, optionally,

(c) an adjunct selected from surfactants, builders, fillers, enzymes, fluorescent whitening agents, pigments, dyes, fragrances, stabilizers and buffers is disclosed. Peracid precursors containing such oxynitrogen leaving groups

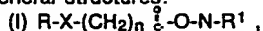
provide new, proficient and cost-effective compounds for fabric bleaching.

EP 0 267 046 A2

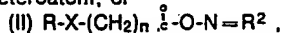
Description

BLEACHING COMPOSITIONS COMPRISING PERACID PRECURSORS

This invention relates to bleaching compositions comprising peracid precursors, more particularly acyloxynitrogen peracid precursors. According to the present invention peroxygen bleach activator compounds that aid in providing efficient peroxygen bleaching of fabrics over a wide temperature range when combined with a source of hydrogen peroxide in aqueous media are utilized. These compounds have the general structures:



wherein R is a straight or branched chain C₁₋₂₀alkyl, alkoxy, cycloalkyl and mixtures thereof; R¹ contains at least one carbon atom which is singly bonded directly to N; n is an integer from 1 to 6 and X is methylene or a heteroatom; or



wherein n is the same as in (I); but R² contains a carbon atom doubly bonded directly to N, and, either X is a heteroatom, R is C₄₋₁₇ alkyl or both.

It is well known that peroxygen bleaches are effective in removing stains and/or soils from textiles. They may be used on a wide variety of fabrics and coloured garments. However, the efficacy of peroxygen bleaches may vary greatly with temperature of the wash water in which they are used and they are usually most effective when the bleaching solution is above 130°F (54°C). Below this temperature, it has been found that peroxide bleaching efficacy may be greatly increased by the simultaneous use of activators, otherwise known as peracid precursors. It has widely been accepted that in aqueous media, precursors and peroxygen combine to form peracid species. However, efficacy of most precursors, such as tetracetylene diamine (TAED), is also dependent on high wash water temperature. However, there is a need for bleach activator or peracid precursor compounds which are able to react with peroxide efficiently at low temperatures (70-100°F; 21-38°C) to form peracids in good yields for proper cleaning performance.

Peracids themselves may be hazardous to make and are particularly prone to decomposition upon long-term storage. Thus it is advantageous to prepare the more stable peracid precursor compounds, which in alkaline water solution will react with peroxide anion to form the desired peracid in situ. As may be seen from the extensive literature in this area, many such peroxygen activators (peracid precursors) have been proposed. However, no reference appears to have taught, disclosed or suggested the advantages of leaving groups containing nitrogen in perhydrolysis.

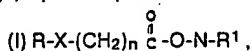
Various compounds have been disclosed in the prior art that contain nitrogen as part of the leaving group of the peroxygen precursors. U.S. Patent Nos. 3,969,257, 3,655,567, 3,061,550 and 3,928,223 appear to disclose the use of acyl groups attached to nitrogen atoms as leaving groups for activators. In all these examples, the acyl carbon atom is directly attached to the nitrogen atom. The nitrogen may in turn be attached to other carbonyl carbon groups.

In U.S. Patent No. 4,164,395, a sulphonyl group is attached to the nitrogen atom of the leaving group. The activator structure is thus a sulphonyl oxime.

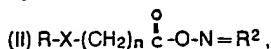
U.S. Patent No. 3,975,153 teaches the use of only isophorone oxime acetate as a bleach activator. It is claimed that this isophorone derivative results in an activator of low odour and low toxicity. In U.S. Patent No. 3,816,319, the use of diacylated glyoximes is taught. The use is restricted to diacylated dialkylglyoximes wherein the alkyl group contains one to four carbon atoms and the acyl group contains two to four atoms. In neither reference is it disclosed, taught or suggested that it is surprisingly necessary to provide a heteroatom alpha to the carbonyl of the acyl group if a peracid precursor contains oxime as a leaving group. Additionally, neither reference discloses the unique advantages conferred by surface active peracid precursors which contain about 4-14 carbons in the acyl group.

In one embodiment, the present invention relates to a bleaching composition comprising:

(a) a peracid precursor having the general structure:



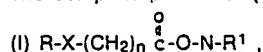
wherein R is a straight or branched chain C₁₋₂₀alkyl, alkoxy, cycloalkyl and mixtures thereof; R¹ contains at least one carbon atom which is singly bonded directly to N; n is an integer from 1 to 6 and X is methylene or a heteroatom; or



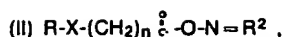
wherein n is the same as in (I); but R² contains a carbon atom doubly bonded directly to N, and either X is a heteroatom, R is C₄₋₁₇ alkyl or both; and

(b) a bleach-effective amount of a source of hydrogen peroxide.

The complete precursor (an ester) is



wherein R is a straight or branched chain C₁₋₂₀alkyl, alkoxy, cycloalkyl and mixtures thereof; R¹ contains at least one carbon atom which is singly bonded directly to N, n is an integer from 1 to 6 and X is methylene or a heteroatom; or



wherein n is the same as in (I); but R¹ contains a carbon atom doubly bonded directly to N, and, either X is a heteroatom, R is C₄₋₁₇ alkyl or both.

It is preferred that R is C₁₋₂₀ alkyl or alkoxyalkyl. More preferably, R is C₄₋₁₇, and mixtures thereof. R may also be mono- or poly-unsaturated. If alkoxyalkyl, ethoxy (EO) -(OCH₂CH₂) and propoxy (PO) -(OCH₂CH₂CH₂) groups are preferred, and may be present, per mole of ester, from 1 to 30 EO or PO groups, and mixtures thereof.

It is preferred for R to be from 4 to 17, and especially from 6 to 12, carbons in the alkyl chain. Such alkyl groups would be surface active and would be desirable when the precursor is used to form surface active peracids for oxidizing fat or oil based soils from substrates at relatively low temperatures.

These alkyl groups are generally introduced onto the ester via an acid chloride synthesis discussed further below. Fatty acid chlorides such as hexanoyl chloride, heptanoyl chloride, octanoyl chloride, nonanoyl chloride and decanoyl chloride, provide this alkyl moiety. When it is desired to introduce an aryl group, an aromatic acid chloride may be used, such as phenoxyacetyl chloride, although this is the subject of concurrently filed applicationentitled "Peroxyacids, Phenoxyacetate Peracid Precursors and Perhydrolysis Systems", (based on USSN 927,856 and USSN 45,197).

Also, in the above generic structures for the present precursors, when n is 1, X is at the alpha-position to the terminal carbonyl group. In the present invention, under certain circumstances, such as when the nitrogen of the oxynitrogen bond is itself double bonded to a carbon atom (structure (II)), forming an oxime, X is O, oxygen. X, however, could also be another electronegative atom, such as -S-(sulphide), -N-(amine) or even -NH⁺ (quaternary ammonium). In accordance with the present invention, however, it is most preferable that X is O (oxygen), or methylene.

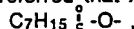
As mentioned, n = 1 to 6 carbonyl substituents, but n = 1 to 3 is more preferred, and most preferably n does not exceed about 2.

When n = 1 or 2, the base carbonyl is an acetic acid or propionic acid derivative. The acetic acid derivatives have been found surprisingly effective and are discussed in two concurrently filed applicationsandentitled "Bleaching Compositions, Glycolate Ester Peracids and Precursors", and "Peroxyacids, Phenoxyacetate Peracid Precursors and Perhydrolysis Systems" (based on USSN 928,070 and USSN 927,856/USSN 45,197, respectively.)

When the heteroatom, X is O (oxygen), and n is 1, the effect of an electronegative substituent alpha to the terminal carbonyl enhances the reactivity of the present precursors.

The electronic effect of this modification at the proximal methylene group (when n = 1) appears to make the carbonyl group more susceptible to nucleophilic attack by a perhydroxide anion. The resulting enhanced reactivity results in higher peracid yields at low temperatures (e.g., 70°F; 21°C), across a broader pH range, and makes the perhydrolysis reaction to generate peracids less susceptible to critical activator to H₂O₂ ratios.

However, in another embodiment, when the leaving group of the precursor is structure (I), -ONR¹, it is preferred that X is methylene. As a representative example, the octanyl group,



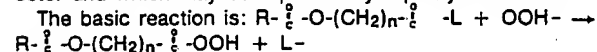
does not contain any heteroatoms within the alkyl chain.

In the following discussion, certain definitions are utilized:

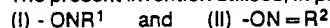
Peracid precursor is generally equivalent to bleach activator. Both terms generally relate herein to reactive esters which have a leaving group substituent, which during perhydrolysis, actually cleave off the acyl portion of the ester.

Perhydrolysis is the reaction which occurs when a peracid precursor or activator is combined in a reaction medium (aqueous medium) with an effective amount of a source of hydrogen peroxide.

The leaving group is basically a substituent which is attached via an oxygen bond to the acyl portion of the ester and which may be replaced by a perhydroxide anion (OOH⁻) during perhydrolysis.

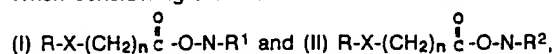


The present invention utilizes, in particular, oxynitrogen leaving groups having the general structures



which are attached to an acyl, R- $\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$ -, group to form the peracid precursors in accordance with the present invention. These leaving groups have an oxygen atom attached to nitrogen which in turn may be attached to carbon atoms in a variety of structural configurations. The oxygen of the leaving group is attached directly to the carbonyl carbon to form the intact precursor.

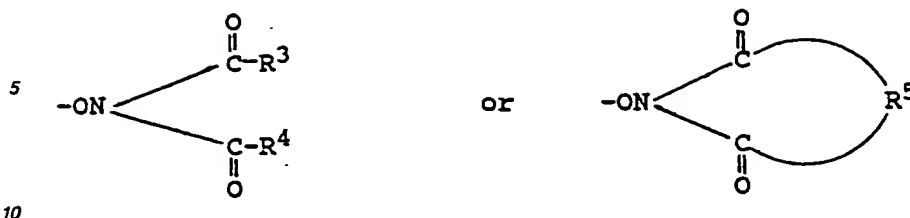
When considering the activator structures below



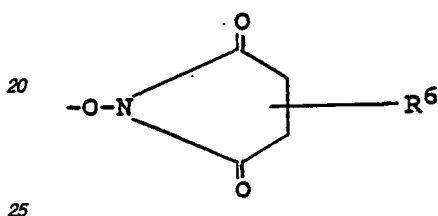
there are at least two different types of structure for the R¹ group and there is at least one type of structure for the R² group.

The first preferred structure for R¹ is where the nitrogen atom is attached to two carbonyl carbon groups.

The leaving group then would be an oxymide group :

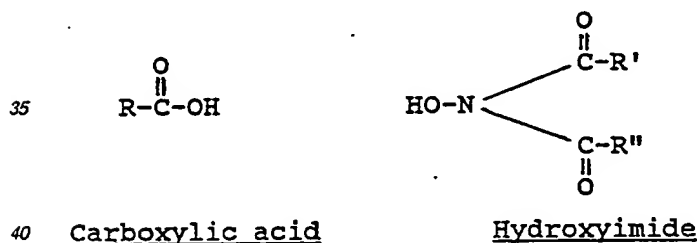


wherein R^3 and R^4 may be the same or different, and are preferably straight chain or branched C 1-20 alkyl, aryl, alkylaryl or mixtures thereof. If alkyl, R^3 and R^4 may be partially unsaturated. It is especially preferred that R^3 and R^4 are straight or branched chain C₁₋₆ alkyls, which may be the same or different. R^5 is preferably C₁₋₂₀alkyl, aryl or alkylaryl, and completes a heterocycle. R^5 includes the preferred structure:



wherein R^6 may be an aromatic ring fused to the heterocycle, or C₁₋₆ alkyl.

Thus, these leaving group structures could contain an acyclic or cyclic oxime moiety. The above precursor may be seen as a combination of a carboxylic acid and a hydroxyimide compound:

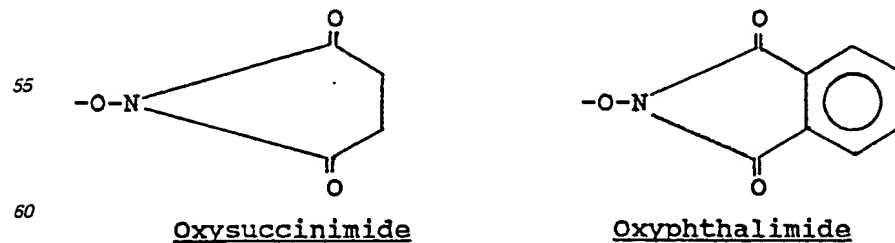


These esters of imides may be prepared as described in Greene, Protective Groups in Organic Synthesis, p. 183, and are generally the reaction products of acid chlorides and hydroxyimides.

Examples of N-hydroxyimides which will provide the oxime leaving groups in accordance with the present invention includes:

N-hydroxysuccinimide, N-hydroxyphthalimide, N-hydroxyglutarimide, N-hydroxynaphthalimide, N-hydroxymaleimide, N-hydroxydiacetylilmide and N-hydroxydipropionylimide.

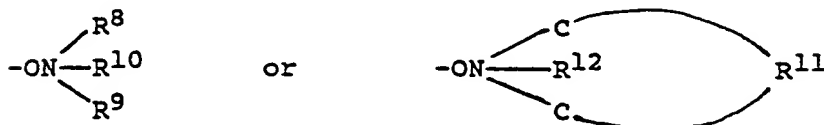
Especially preferred examples of oxime leaving groups are:



When treated with peroxide anion, a peracid is formed and the leaving group departs with oxygen attached to nitrogen and a negative charge on the oxygen atoms. The pKa (about 6) of the resulting hydroxyimides is

quite low, making them excellent leaving groups.

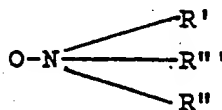
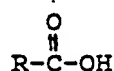
The second preferred structure for R¹ is where the nitrogen atom is attached to at least two carbons. These are amine oxide leaving groups, comprising:



In the first preferred structure for amine oxides, R⁸ and R⁹ may be the same or different, and are preferably C₁₋₂₀ straight or branched chain alkyl, aryl, alkylaryl or mixtures thereof. If alkyl, the substituent may be partially unsaturated. Preferably, R⁸ and R⁹ are C₁₋₄alkyls and may be the same or different. R¹⁰ is preferably C₁₋₃₀ alkyl, aryl, alkylaryl and mixtures thereof. This R¹⁰ substituent may also be partially unsaturated. It is most preferred that R⁸ and R⁹ are relatively short chain alkyl groups (CH₃ or CH₂CH₃) and R¹⁰ is preferably C₁₋₂₀ alkyl, forming together a tertiary amine oxide.

Furthermore, in the second preferred amine oxide structure, R¹¹ may be C₁₋₂₀ alkyl, aryl or alkylaryl, and completes a heterocycle. R¹² preferably completes an aromatic heterocycle of 5 carbon atoms and may be C₁₋₆alkyl or aryl substituted. R¹² is preferably nothing, C₁₋₃₀ alkyl, aryl, alkylaryl or mixtures thereof. R¹² is more preferably C₁₋₂₀ alkyl if R¹¹ completes an aliphatic heterocycle. If R¹¹ completes an aromatic heterocycle, R¹² is nothing.

This type of structure is really a combination of a carboxylic acid and an amine oxide:



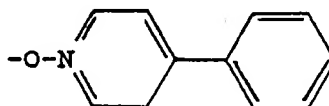
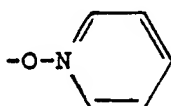
Carboxylic acid

Amine oxide

Amine oxides may be prepared as described in March, Advanced Organic Chemistry, 2d Ed., 1977, p.1,111.

Examples of amine oxides suitable for use as leaving groups may be derived from: pyridine N-oxide, trimethylamine N-oxide, 4-phenyl pyridine N-oxide, decyldimethylamine N-oxide, dodecyldimethylamine N-oxide, tetradecyldimethylamine N-oxide, hexadecyldimethylamine N-oxide, octyldimethylamine N-oxide, di(decyl)methylamine N-oxide, di(dodecyl)methylamine N-oxide, di(tetradecyl)methylamine N-oxide, 4-picoline N-oxide, 3-picoline N-oxide and 2-picoline N-oxide.

Especially preferred amine oxide leaving groups include:



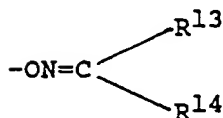
Pyridinium N-oxide

Phenylpyridinium N-oxide

When the precursor is attacked by peroxide anion, a peracid is formed and the leaving group leaves as an amine oxide, again with oxygen attached to nitrogen and the negative charge on the oxygen.

When the oxynitrogen leaving group is structure (II) -ON = R², preferred examples thereof are oximes.

In these oxime leaving groups, the nitrogen atom is attached to a carbon atom via a double bond.



wherein R¹³ and R¹⁴ are individually H, C₁₋₂₀ alkyl, (which may be cycloalkyl, straight or branched chain), aryl, or alkylaryl. Preferably R¹³ and R¹⁴ are the same or different and range from C₁₋₆; and at least one of R¹³ and

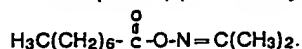
R¹⁴ is not H.

The structure of an oxime ester of a carboxylic acid may be broken down into two parts:

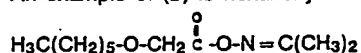


As mentioned above, since R² comprises carbon double bonded directly to the nitrogen of the oxynitrogen bond, either (a) the R group of the acyl is preferably C₄₋₁₇, more preferably C₆₋₁₂, alkyl (resulting in a surface active ester) or (b) X, the heteroatom is oxygen and the carbylene number, n, is 1, or (c) both conditions may occur.

An example of (a) is octanoyloxy dimethyl oxime ester,



An example of (b) is hexanoxy acetyl dimethyl oxime ester,



Oximes are generally derived from the reaction of hydroxylamines with either aldehydes or ketones (Allinger et al, Organic Chemistry, 2d Ed., p.562 (1976), both of which are within the scope of the present invention.

Examples of an oxime leaving group are: (a) oximes of aldehydes (aldoximes), e.g., acetaldoxime, benzaldoxime, propionaldoxime, butylaldoxime, heptaldoxime, phenylacetaldoxime, p-tolualdoxime, anisaldoxime, caproaldoxime, valeraldoxime and p-nitrobenzaldoxime; and (b) oximes of ketones (ketoximes), e.g., acetone oxime (2-propanone oxime), methyl ethyl ketoxime (2-butanone oxime), 2-pentanone oxime, 2-hexanone oxime, 3-hexanone oxime, cyclohexanone oxime, acetophenone oxime, benzophenone oxime, and cyclopentanone oxime.

Particularly preferred oxime leaving groups are:



When attacked by peroxide anion, the oxime ester forms a peracid and the oxime becomes the leaving group. It is rather surprising that the oximes are such good leaving groups since their pK_a values (about 12) are rather high for a good leaving group. Previous experience teaches that leaving groups with pK_a values for their conjugate acids in the 8-10 range make the best leaving groups. Although there are examples in the prior art of oxime esters (U.S. Patent Nos. 4,164,395 and 3,975,153), in fact, no mention is made that a heteroatom alpha to the carbonyl group on the acyl portion of the ester is necessary for good perhydrolysis yields; or that if the R group of the acyl is C₄₋₁₇ alkyl, more preferably C₆₋₁₂alkyl, surface active peracid precursors giving rise to surface active peracids will result.

The present precursors may be incorporated into a liquid or solid matrix for use in liquid or solid detergent bleaches by dissolving into an appropriate solvent or surfactant or by dispersing liquid or liquified precursors onto a substrate material, such as an inert salt (e.g., NaCl, Na₂SO₄) or other solid substrate, such as zeolites, sodium borate, or molecular sieves. Examples of appropriate solvents include acetone, non-nucleophilic alcohols, ethers or hydrocarbons.

Other more water-dispersible or -miscible solvents may be considered. As an example of affixation to a substrate material, the present precursors could be incorporated onto a non-particulate substrate such as disclosed in published European Patent Application EP 98 129.

The present precursors with oxynitrogen leaving groups are apparently not as soluble in aqueous media as phenyl sulphonates. Thus, a preferred embodiment of the present invention is to combine the precursors with a surfactant. It is particularly preferred to coat these precursors with a nonionic or anionic surfactant that is solid at room temperature and melts at above about 40° C. A melt of surfactant may be simply admixed with peracid precursor, cooled and chopped into granules. Exemplary surfactants for such use are illustrated in Table I below:

Table I

<u>Commercial Name</u>	<u>m.p.</u>	<u>Type</u>	<u>Supplier</u>
Pluronic F-98	55°C	Nonionic	BASF Wyandotte
Neodol 25-30	47°C	Nonionic	Shell Chemical
Neodol 25-60	53°C	Nonionic	Shell Chemical
Tergitol-S-30	41°C	Nonionic	Union Carbide
Tergitol-S-40	45°C	Nonionic	Union Carbide
Pluronic 10R8	46°C	Nonionic	BASF Wyandotte
Pluronic 17R8	53°C	Nonionic	BASF Wyandotte
Tetronic 90R8	47°C	Nonionic	BASF Wyandotte
Amidox C5	55°C	Nonionic	Stepan

The precursors, whether coated with the surfactants with melting completion temperatures above about 40°C or not so coated, could also be admixed with other surfactants to provide, depending on formulation, either bleach additive or detergent compositions.

Particularly effective surfactants appear to be nonionic surfactants. Preferred surfactants for use include linear ethoxylated alcohols, such as those sold by Shell Chemical Company under the brand name Neodol. Other suitable nonionic surfactants may include other linear ethoxylated alcohols with an average length of 6 to 16 carbon atoms and averaging about 2 to 20 moles of ethylene oxide per mole of alcohol; linear and branched, primary and secondary ethoxylated, propoxylated alcohols with an average length of about 6 to 16 carbon atoms and averaging 0-10 moles of ethylene oxide and about 1 to 10 moles of propylene oxide per mole of alcohol; linear and branched alkylphenoxy (polyethoxy) alcohols, otherwise known as ethoxylated alkylphenols, with an average chain length of 8 to 16 carbon atoms and averaging 1.5 to 30 moles of ethylene oxide per mole of alcohol; and mixtures thereof.

Further suitable nonionic surfactants may include polyoxyethylene carboxylic acid esters, fatty acid glycerol esters, fatty acid and ethoxylated fatty acid alkanolamides, certain block copolymers of propylene oxide and ethylene oxide, and block polymers of propylene oxide and ethylene oxide with propoxylated ethylene diamine. Also included are such semi-polar nonionic surfactants as amine oxides, phosphine oxides, sulfoxides, and their ethoxylated derivatives.

Anionic surfactants may also be suitable. Examples of such anionic surfactants may include the ammonium, substituted ammonium (e.g., mono-, di-, and triethanolammonium), alkali metal and alkaline earth metal salts of C₈-C₂₀ fatty acids and rosin acids, linear and branched alkyl benzene sulphonates, alkyl sulphates, alkyl ether sulphates, alkane sulphonates, olefin sulphonates, hydroxyalkane sulphonates, fatty acid monoglyceride sulphates, alkyl glyceryl ether sulphates, acyl sarcosinates and acyl N-methyltaurides.

Suitable cationic surfactants may include the quaternary ammonium compounds in which typically one of the groups linked to the nitrogen atom is a C₁₂-C₁₈ alkyl group and the other three groups are short chained alkyl groups which may bear inert substituents such as phenyl groups.

Furthermore, suitable amphoteric and zwitterionic surfactants which contain an anionic water-solubilizing group, a cationic group and a hydrophobic organic group may include amino carboxylic acids and their salts, amino dicarboxylic acids and their salts, alkylbetaines, alkyl aminopropylbetaines, sulphobetaines, alkyl imidazolinium derivatives, certain quaternary ammonium compounds, certain quaternary phosphonium compounds and certain tertiary sulphonium compounds. Other examples of potentially suitable zwitterionic surfactants may be found described in U.S. Patent No. 4,005,029, at columns 11-15.

Further examples of anionic, nonionic, cationic and amphoteric surfactants which may be suitable for use in accordance with the present invention are depicted in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 22, pages 347-387, and McCutcheon's Detergents and Emulsifiers, North American Edition, 1983.

As mentioned above, other common detergent adjuncts may be added if a bleach or detergent bleach product is desired. If, for example, a dry bleach composition is desired, the following ranges (weight %) appear practicable:

0.5-50.0%	Hydrogen Peroxide Source
0.05-25.0%	Precursor
1.0-50.0%	Surfactant
1.0-50.0%	Buffer
5.0-99.9%	Filler, stabilizers, dyes, fragrances, brighteners, etc.

The hydrogen peroxide source may be selected from the alkali metal salts of percarbonate, perborate, persulfate and hydrogen peroxide adducts and hydrogen peroxide. Most preferred are sodium percarbonate,

sodium perborate mono- and tetra-hydrate, and hydrogen peroxide. Other peroxygen sources may be possible, such as monopersulphates and monoperphosphates. In liquid applications, liquid hydrogen peroxide solutions are preferred, but the precursor may need to be kept separate therefrom prior to combination in aqueous solution to prevent premature decomposition.

5 The range of peroxide to peracid precursor is preferably determined as a molar ratio of peroxide to ester groups contained in the precursor. Thus, the range of peroxide to each ester group is preferably a molar ratio of from about 0.5 to 10:1, more preferably about 1:1 to 5:1 and most preferably about 1:1 to 2:1. It is preferred that this peracid precursor/peroxide composition provide preferably about 0.5 to 100 ppm A.O., and most preferably about 1 to 50 ppm A.O., and most preferably about 1 to 20 ppm A.O., in aqueous media.

10 A description and explanation of A.O. measurement is to be found in the article of Sheldon N. Lewis, "Peracid and Peroxide Oxidations", In: Oxidation, 1969, pp. 213-258. Determination of the peracid may be ascertained by the analytical techniques taught in Organic Peracid, (Ed. by D. Swern), Vol. 1, pp. 501 et seq. (CH.7) (1970).

15 An example of a practical execution of a liquid delivery system is to dispense separately metered amounts of the precursor (in some non-reactive fluid medium) and liquid hydrogen peroxide in a container such as described in U.S. Patent No. 4,585,150.

A buffer may be selected from sodium carbonate, sodium bicarbonate, sodium borate, sodium silicate, phosphoric acid salts, and other alkali metal/alkaline earth metal salts known to those skilled in the art. Organic buffers, such as succinates, maleates and acetates may also be suitable for use. It appears preferable to have 20 sufficient buffer to attain an alkaline pH, i.e., above at least about 7.0, more preferably above about pH 9.0, and most preferably above about pH 10.0.

The filler material, which, in a detergent bleach application, may actually constitute the major constituent, by weight, of the detergent bleach, is usually sodium sulphate. Sodium chloride is another potential filler. Dyes include anthraquinone and similar blue dyes. Pigments, such as ultramarine blue (UMB), may also be used, 25 and may have a bluing effect by depositing on fabrics washed with a detergent bleach containing UMB. Monostral colourants are also possible for inclusion. Brighteners, such as stilbene, styrene and styrylnaphthalene brighteners (fluorescent whitening agents), may be included. Fragrances used for aesthetic purposes are commercially available from Norda, International Flavors and Fragrances and Givaudon. Stabilizers include hydrated salts, such as magnesium sulphate, and boric acid.

30 In one of the preferred embodiments in which a compound such as in (I) below is the precursor, a preferred bleach composition has the following ingredients:

35	12.8%	Sodium Perborate Tetrahydrate
	8.3%	Octanoyloxy dimethyl oxime ester
	7.0%	Nonionic surfactant
	15.0%	Sodium Carbonate
40	<u>56.9%</u>	Sodium Sulphate
	100.0%	

45 In another of the preferred embodiments, in which a compound as in (II) below is the precursor, a preferred bleach composition has the following ingredients:

50	12.8%	Sodium Perborate Tetrahydrate
	10.0%	Octanoyloxy succinimide
	7.0%	Nonionic surfactant
	15.0%	Sodium Carbonate
55	<u>55.2%</u>	Sodium Sulphate
	100.0%	

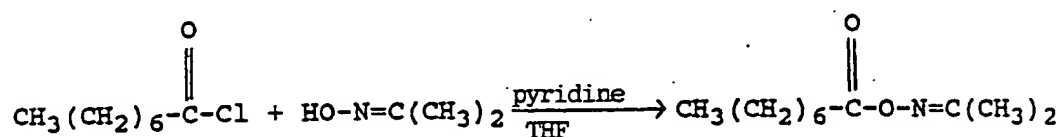
60 Other peroxygen sources, such as sodium perborate monohydrate or sodium percarbonate are suitable. If a more detergent-type product is desired, the amount of filler may be increased and the precursor halved or further decreased.

65

EXPERIMENTAL

The oxime esters may be prepared by treatment of an oxime with the acid chloride of the corresponding carboxylic acid. In order to have a liquid reaction medium, a non-reactive solvent is added, and a base.

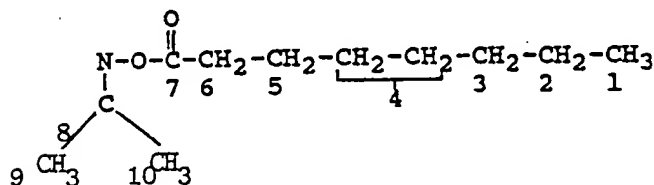
The oximes may be purchased or prepared by treatment of a carbonyl compound with hydroxylamine. Two oximes, acetone oxime and methyl ethyl ketone oxime are readily available from commercial sources and are inexpensive.

EXAMPLE I**Preparation of Acetone Oxime Ester of Octanoic Acid**

A 500 ml three-neck flask was fitted with a paddle stirrer, condenser and dry tube, and lowered into an oil bath. To the flask was added THF (100 ml), acetone oxime (15g, 0.21 mole), pyridine (16.5 ml, 0.21 mole), and then octanoyl chloride (35 ml, 0.21 mole) in THF (50 ml), dropwise, with rapid stirring. A white solid (pyridine hydrochloride) precipitated from the solution. The reaction was allowed to stir in an oil bath at a temperature of 50°C for three hours. The reaction mixture was filtered and the solvent therein removed via roto-evaporator to give an orange oil (38.8g).

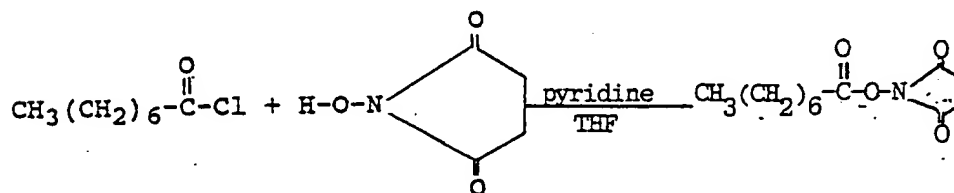
Thin layer chromatography analysis (silica gel, HX-ETAC, 80-20) of the crude product showed one main spot (I_2 visualization) at $R_f = .47$, a small spot at $R_f = .90$ and a spot at the origin, probably pyridine hydrochloride. The crude product was placed on a column of silica gel (125g, 230-400 mesh, 4cm D x 25 cm H) and eluted with HX-ETAC (80-20). The fractions were monitored by TLC, the appropriate ones combined and solvent removed. In this way, 37.8g of a colourless oil was obtained.

The infrared spectrum of the oil gave a very strong carbonyl at 1768 cm^{-1} and showed no sign of hydroxyl, acid chloride, or carboxylic acid. The ^{13}C -NMR (CDCl_3 , ppm downfield from TMS) showed only absorptions expected for the product. Using the numbering system shown, these assignments are made:



$\text{C}_7(168.3)$, $\text{C}_8(160.9)$, $\text{C}_3(29.9)$, $\text{C}_6(30.8)$, $\text{C}_4(27.2)$, $\text{C}_5(23.0)$, $\text{C}_2(20.7)$, $\text{C}_9(19.6)$, $\text{C}_{10}(12.0)$, and $\text{C}_1(14.5)$.

The acyloxyimides may be readily prepared by the treatment of a hydroxyimide with an acid chloride. While the acid chlorides are readily, commercially available, the hydroxyimides are not so commercially available.

EXAMPLE II**Preparation of Octanoyloxy Succinimide**

A 500 ml three-neck flask was fitted with double stirrer, condenser with drying tube, and lowered into an oil bath. To the flask was added THF (175 ml), the N-hydroxysuccinimide (9.5 g, 0.083 mole) and pyridine (6.7 ml, 0.083 mole). Octanoyl chloride (14.2 ml, 0.083 mole) was dissolved in THF (50 ml) and added to the reaction

vessel over a period of 15 minutes. A white precipitate (pyridine hydrochloride) formed. The reaction mixture was heated at about 60°C for 3 hours, filtered, the solvent removed via roto-evaporator to give a light yellow oil (18.9g), which subsequently solidified.

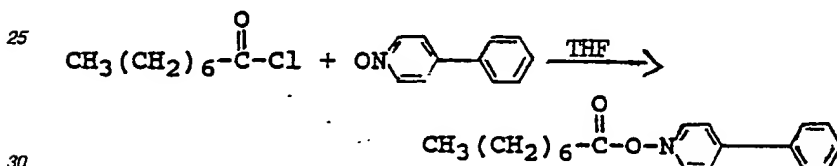
Thin-layer chromatography analysis (silica gel, CH₂Cl₂) of the crude oil showed a main spot at R_f = .60 (UV visualization), a small spot at R_f = .95 and a spot at the origin (pyridine hydrochloride). The crude product was placed on a column of silica gel (150g, 230-400 mesh, 4 cm diameter × 30 cm tall) and eluted with methylene chloride. The fractions were monitored by TLC, the appropriate ones combined, and the solvent removed. Thus, a white solid (15.2 g, 76% yield) of m.p. 60.5-61.0°C was obtained.

The infrared spectrum of this solid gave a very strong broad carbonyl at 1735 cm⁻¹ and sharp ones at 1790 and 1822 cm⁻¹. The ¹³C-NMR (CDCl₃) was very clean, showing only those absorptions necessary for the product. Thus it showed ester carbonyl carbon at 169.5 (ppm downfield from TMS), imide carbonyl at 170.0 and the methylene and methyl carbons at 14.0-31.6 ppm. Analysis of the solid by saponification number gave a purity of 100%.

The acyl oxy ammonium chloride type compounds MAY be prepared by treatment of an amine oxide with an acid chloride. Both amine oxides and acid chlorides are readily available commercially so this should provide for a large variety of practical precursors. However, the product appears to be formed as a nice solid only when certain high molecular weight amine oxides are used. Unless care is taken in selecting the reaction conditions and the reagents, the reaction may at times form oils.

20 EXAMPLE III

Preparation of Octanoyloxy Ester of 4-Phenylpyridine Oxide

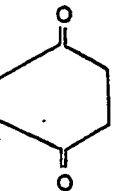
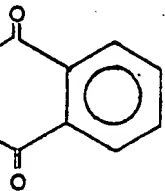
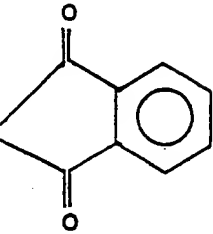
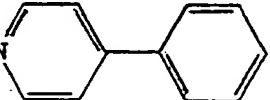


A 500 ml three-neck flask was fitted with a paddle stirrer, drying tube, and flushed with nitrogen.

35 To the flask was added THF (150 ml) and 4-phenylpyridine N-oxide (5g, 0.029 mole). A light yellow solution resulted. To this was added rapidly octanoyl chloride (5.0 ml, 0.029 mole) in THF (20 ml). The mixture was stirred very rapidly for 1 1/2 minutes. A gelatinous precipitate formed almost immediately. When the viscous solution was diluted with ether (about 300 ml), a white solid layer separated. The mix was filtered to give a white solid which was washed with ether. The dried white solid (7.0 g, 72% yield) had a carbonyl absorption at 1822 cm⁻¹ in the infrared spectrum. The ¹³C-NMR was very clean and showed only those absorptions necessary for the product. A carbonyl at 174.5 (DMSO solvent, ppm downfield from TMS) was observed in addition to absorptions for the aromatic carbons and those for the alkyl chain.

When treated with alkaline, aqueous peroxide anion, the precursors described formed peracids in solution. The table below summarizes the perhydrolysis yields of typical precursors.

Table I

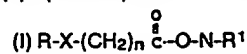
<u>Item</u>	<u>Structure</u>	<u>% Peracid Yield*</u>
1	$\text{CH}_3(\text{CH}_2)_6\text{C}(=\text{O})\text{O}-\text{N}=\text{C}(\text{CH}_3)_2$	46%
2	$\text{CH}_3(\text{CH}_2)_6\text{C}(=\text{O})\text{O}-\text{N}=\text{C}\begin{matrix} \text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{matrix}$	37%
3	$\text{CH}_3(\text{CH}_2)_6\text{C}(=\text{O})\text{O}-\text{N}$ 	90%
4	$\text{CH}_3(\text{CH}_2)_6\text{C}(=\text{O})\text{O}-\text{N}$ 	86%
5	$\text{CH}_3(\text{CH}_2)_6\text{C}(=\text{O})\text{O}-\text{CH}_2-\text{N}$ 	none
6	$\text{CH}_3(\text{CH}_2)_6\text{C}(=\text{O})\text{O}-\text{N}$ 	21%

* pH 10.5, 5 min, 70°F (21°C) 2:1 peroxide: activator molar ratio, Pluronic L63 surfactant (0.1 wt %)

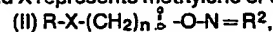
A comparison of item 5 with all the others, shows the importance of having the oxygen atom attached directly to nitrogen atom of the leaving group, in accordance with the teachings of the present invention.

Claims

1. A bleaching composition characterised in that it comprises:
 (a) a peracid precursor corresponding to the following general formula:



wherein R represents C₁-C₂₀ alkyl, alkoxy, or cycloalkyl; R¹ represents a group which contains at least one carbon atom which is singly bonded directly to N; n represents an integer of from 1 to 6; and X represents methylene or a heteroatom; or



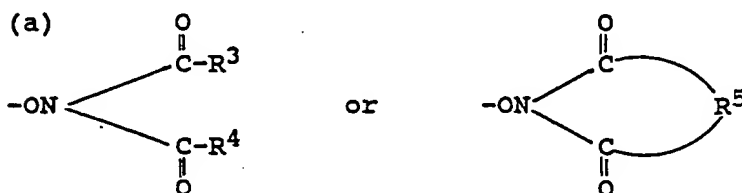
wherein n is as defined above; R² represents a group which contains a carbon atom doubly bonded directly to N, and, either X represents a heteroatom, R represents C₄-C₁₇ alkyl, or both;

(b) a bleach-effective amount of a source of hydrogen peroxide;

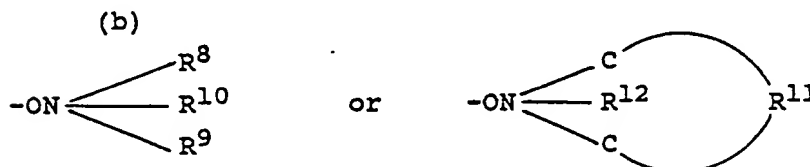
and, optionally,

(c) an adjunct selected from surfactants, builders, fillers, enzymes, fluorescent whitening agents, pigments, dyes, fragrances, stabilizers and buffers.

2. A bleaching composition as claimed in claim 1 wherein the peracid precursor (I) comprises a leaving group -O-N-R¹ which is either



wherein R³ and R⁴ independently represent C₁-C₂₀ alkyl, aryl or alkylaryl; and R⁵ represents C₁-C₂₀ alkyl, aryl or alkylaryl and completes a heterocycle; or

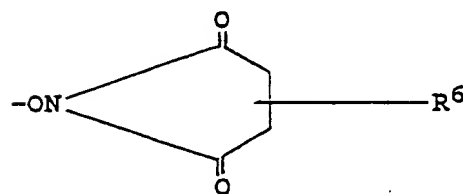


wherein R⁸ and R⁹ independently represent C₁-C₂₀ alkyl, aryl or alkylaryl; R¹⁰ represents C₁-C₃₀ alkyl, aryl or alkylaryl; R¹¹ represents C₁-C₂₀ alkyl, aryl, alkylaryl and completes a heterocycle; and R¹² represents nothing, C₁-C₂₀ alkyl, aryl or alkylaryl.

3. A bleaching composition as claimed in claim 1 or claim 2 wherein R represents C₆-C₁₂ alkyl, X represents methylene, and n represents 1.

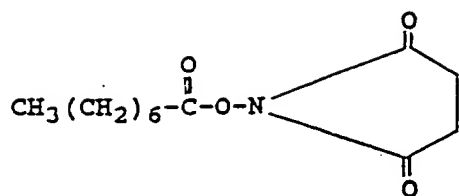
4. A bleaching composition as claimed in claim 2 or claim 3 wherein the leaving group is (a) and the precursor is an oximide ester.

5. A bleaching composition as claimed in claim 4 wherein the precursor has the leaving group:

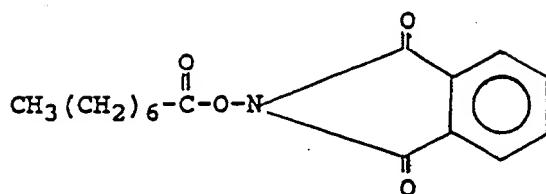


wherein R⁶ represents methylene, an aromatic ring fused to the heterocycle, or C₁-C₆ alkyl.

6. A bleaching composition as claimed in any of claims 1 to 5 wherein the precursor is:

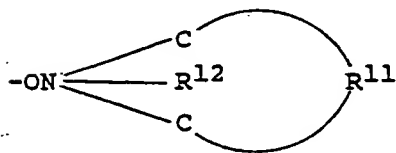


or



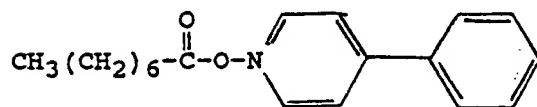
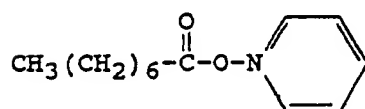
7. A bleaching composition as claimed in claim 2 or claim 3 wherein the leaving group is (b) and the precursor is an amine oxide ester.

8. A bleaching composition as claimed in claim 7 wherein the precursor has the leaving group:



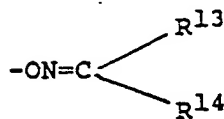
wherein R¹¹ completes an aromatic heterocycle and R¹² represents nothing.

9. A bleaching composition as claimed in claim 8 wherein the precursor is:



10. A bleaching composition as claimed in claim 1 or claim 2 wherein X represents oxygen and n represents 1.

11. A bleaching composition as claimed in claim 1 wherein the peracid precursor (II) comprises a leaving group -ON=R² which is:

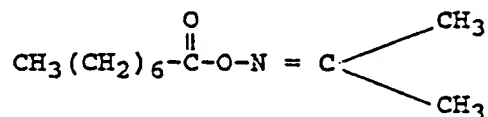


wherein R¹³ and R¹⁴ independently represent H, C₁-C₂₀ alkyl, aryl or alkylaryl, not both R¹³ and R¹⁴ representing H; and (a) R represents C₄-C₁₇ alkyl, (b) X represents oxygen and n represents 1, or (c)

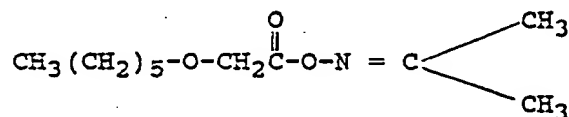
both.

12. A bleaching composition as claimed in claim 11 wherein R represents C₆-C₁₂ alkyl, and R¹³ and R¹⁴ independently represent H or C₁-C₆ alkyl.

13. A bleaching composition as claimed in claim 11 or claim 12 wherein the precursor is an oxime ester in accordance with (a):



or in accordance with (b):



14. A bleaching composition as claimed in any of claims 1 to 13 wherein the source of hydrogen peroxide (b) is selected from hydrogen peroxide, hydrogen peroxide adducts, alkali metal and alkaline earth metal perborates.

15. A bleaching composition as claimed in claim 14 wherein the hydrogen peroxide source is an alkali metal perborate selected from the mono- and tetra-hydrate forms of sodium perborate.

16. A bleaching composition as claimed in any of claims 1 to 15 wherein the molar ratio of hydrogen peroxide source to precursor is from 0.5:1 to 10:1, based on moles of H₂O₂:moles of ester.

17. A bleaching composition as claimed in any of claims 1 to 16 wherein the precursor (a) is coated with a surfactant having a melting completion temperature above about 40° C.

18. A process for the production of a bleaching composition as defined in any of claims 1 to 17 characterised in that it comprises mixing the constituents.

19. A process for bleaching characterised in that it comprises contacting a material to be bleached with a bleaching composition as defined in any of claims 1 to 17 in aqueous medium.